

**PHOTOINITIATED POLYMERIZATION OF A DENTAL FORMULATION:
1. INFLUENCE OF PHOTOINITIATING SYSTEM, TEMPERATURE
AND LUMINOUS INTENSITY**

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ABSTRACT

The photoinitiated polymerization of a dental formulation is composed of Mixture of monomers 75%Bis-GMA/25%TEGDMA and CQ/DMAEMA as radical photoinitiator was studied by using isothermal photocalorimetry. The effect of temperature, light intensity and photoinitiating system concentration on reaction was investigated. A maximum conversion was obtained for a photoinitiator system concentration of 1% (w/w) and for the highest light intensity studied. It should be noted that a correlation between the glass transition temperature of the final polymer and the conversion has been studied.

Keywords: dental composite; photopolymerization; dimethacrylate resin; photoinitiator system.

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1. INTRODUCTION

The systems of polymerization induced by photochemical were widely developed these last ten years [1-3]. The development is largely due to the simplicity of implementation which represents this technique, but also thanks to the elaboration of successful (performing) formulation [4-6].



The development of a photosensitive dental composite resin [7], results from a knowledge which takes into account not only the quantum yield of the photoinitiator (linked to the wavelength of the light) [8], the chemical nature and the functionality of the monomer [9,10], the fillers and the additives [11], but also to understand well that during the photopolymerization of composite resins, the transformation of the initially viscous material, into a polymer network strongly crosslinked is usually accompanied by one increase of the viscosity and characteristic phenomena appear [12,13]: autoacceleration at the beginning of polymerization [14,15], limited conversion of polymerizable functions [16], propagation and termination reactions controlled by diffusion [17], and volume shrinkage [18]. This complex process and the high rate of this reaction As well as the exothermic effect resulting from the reaction may be the cause of defects in the final material. [19,20]. These heterogeneities alter greatly the physical properties of ultimate products.

We propose, using the Photocalorimetry (photo-DSC), studied the photoinitiated polymerization of a dental formulation composed of a mixture of the Bis-GMA / TEGDMA monomers and a CQ / DAMEMA photoinitiator system. This formulation is the basic resin of many dental composites. The effect of temperature, photoinitiator concentration and light intensity on reaction was investigated in order to optimize the experimental conditions of the reaction and to control the homogeneity of the tridimensional crosslinked polymer network performed.

2. PROTOCOLE EXPÉRIMENTAL

Materials

2,2-bis[4-(2-hydroxy-3-methacryloyloxyprop-1-oxy)phenyl]propane (Bis-GMA,98%) and triethylene glycol dimethacrylate (TEGDMA, 95%, containing 200 p.p.m. of monomethylether hydroquinone) were used as a monomer and reactive diluent, respectively. The photoinitiating system was a mixture of camphoroquinone (CQ, >98%) and 2-(dimethylamino)ethyl methacrylate (DMAEMA, 99%), used in a 1/1 (w/w) ratio. All of these components were purchased from Aldrich (Lyon, France) and used as received without further purification. Figure 1 shows the chemical formulas of the reactants used.

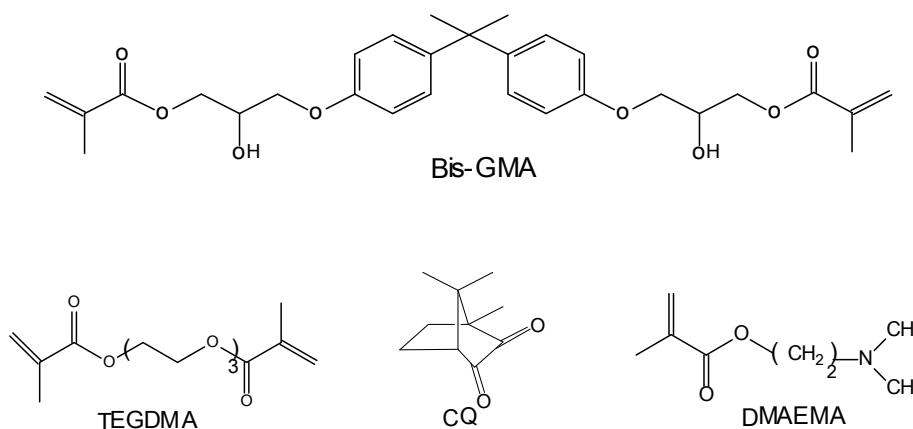


Fig.1. Chemical formulas of reactants

Preparation of the photopolymerizable formulation

The dental formulations were prepared by the mixture of monomer (75% Bis-GMA/25% TEGDMA). Then, the photoinitiating system CQ / DMAEMA (1/1) (w/w) was added at different concentration going from 0,5 to 1,5% by weight relative to the reaction mixture. The whole was heated in the dark for 30 min at 50 ° C using a magnetic stirrer. The obtained formulations are kept in the cold and shielded from the light before their use to avoid any crosslinking reaction.

Analysis Techniques

The Photocalorimeter (Photo-DSC) used to track photopolymerization kinetics is a differential scanning calorimeter (DSC7 Perkin Elmer, Waltham, MA, USA) surmounted by a dental office halogen lamp (LA500 Blue Light, Philippines Union Commercial Inc. , New Manila, Quezon City, Philippines), emitting quasi-monochromatic radiation at 465 nm. The analysis consists of recording the heat flux resulting from the photochemical reaction initiated under irradiation as a function of time at a temperature and under a controlled atmosphere (nitrogen). The intensity of the radiation is measured at the level of the sample (Amprobe LM-100, Glottertal, Germany).

The experiments are carried out on small quantities of samples (exactly 2 mg). The optical part of the calorimeter, sample preparation and treatment of the thermogram were described elsewhere [16].

The area of the registered thermogram (figure 2) quantify the photochemical event and is directly proportional to the quantity of functions having reacted in the reaction medium. We can so determine for a given temperature the following parameters:

- The enthalpy of the reaction (ΔH , in J / g), which is directly proportional to the number of reacted methacrylate double bonds;
- The conversion (C, en %);
- The reaction rate (R_p in s^{-1}).

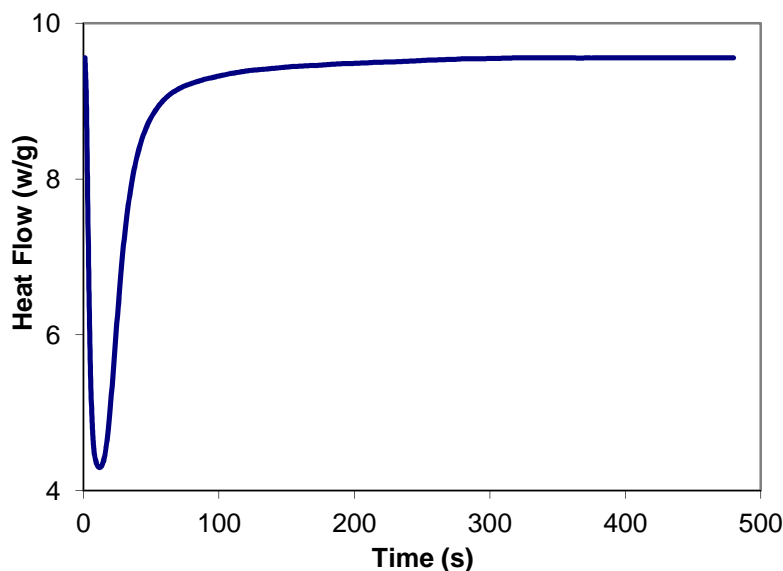


Fig.2. Thermogram type of photopolymerization system
75% Bis-GMA/25% TEGDMA at $T=50^{\circ}\text{C}$.

The conversion C_t is determined from the relation

$$C_t = \frac{\Delta H_t}{\Delta H_{theoretical}} \times 100 \quad (1)$$

Where ΔH_t represents the enthalpy of the reaction at the moment t and $\Delta H_{theoretical}$ represents the theoretical enthalpy which the totality of the methacrylate functions should give. This value is given by the following relation [21]:

$$\Delta H_{theoretical} = \frac{1}{MW_m} \cdot E \cdot f \quad (2) \quad \text{with} \quad MW_m = \left(\frac{w_1}{MW_1} + \frac{w_2}{MW_2} \right)^{-1}$$

Where MW_m : Is the average molar mass of the monomers, E : Is the energy required to break a double bond (for methacrylate functions, $E = -54,7$ kJ/mol) and f : Is the functionality of the monomer ($f = 2$), w_i : Is the mass fraction of each monomer..

Moreover, the polymerization rate was directly connected to the heat flow according to

$$R_p = \frac{dC}{dt} = \frac{d(\Delta H_t)/dt}{\Delta H_{theoretical}} \quad (3)$$

Photocrosslinked samples were analysed by d.m.a. (DMA 7 Perkin-Elmer) in compression mode between two parallel plates with a 1 mm diameter probe at 1 Hz frequency and 5°C min⁻¹ heating rate. The dynamic and static forces applied were respectively 350 and 450 mN. The glass transition temperature T_g was determined at the onset of the storage modulus which is the beginning of the mechanical transition.

3. RESULTS AND DISCUSSION

Influence of the photoinitiator system

The influence of the photoinitiator system on the photopolymerization reaction was studied at 30 ° C. under irradiation of 100 mW / cm² on formulations containing Bis-GMA and TEGDMA (75/25% by mass) and in the presence of different Concentrations ranging from 0.5 to 1.25% by weight of the CQ / DMAEMA equimolar photoinitiator system (figure 3).

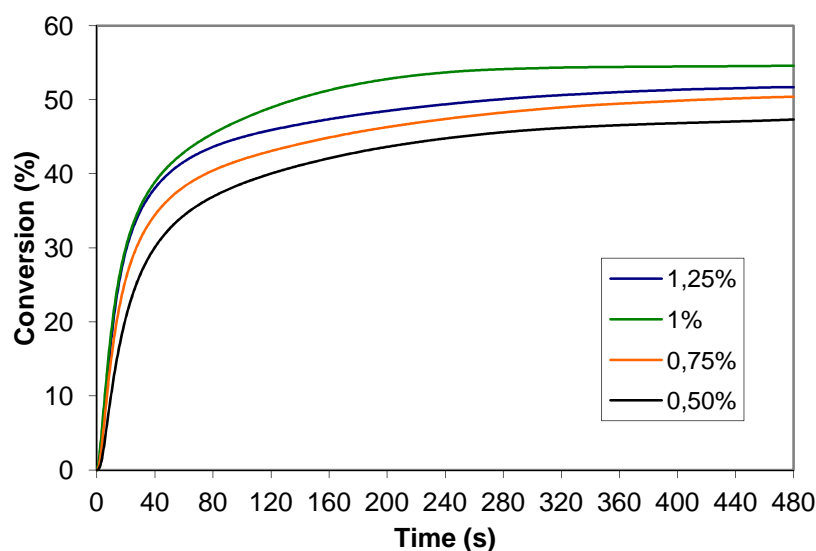


Fig.3. Evolution of the conversion according to the time for different concentrations in the photoinitiator system

We notice that the conversion increases with the concentration in CQ / DMAEMA until 1% (Figure 3). This result is in agreement with the literature [23-25]. The reduction in conversion is generally attributed to the reaction ending of the growing radicals with the primary radicals (stemming from the decomposition of the photoinitiator) present in very large numbers or by recombination of the primary radicals, which corresponds in fact to a decrease of the quantum yield of initiation a.

Influence of light intensity

The study of the photopolymerization of the formulation Bis-GMA/TEGDMA + 1% CQ/DMAEMA (1/1) at 30°C for the five intensities 10, 21, 40, 64 and 228 mW/cm² (figure 4) shows that the conversion and the speed of polymerization increase with the intensity of irradiation. We find in the literature a similar observation by different authors [16, 26, 27]. This is attributed to the increase of the rate of decomposition of the photoinitiator and therefore to the amount of primary radicals formed. It results then an increase of the rate of initiating of the macromolecular chains.

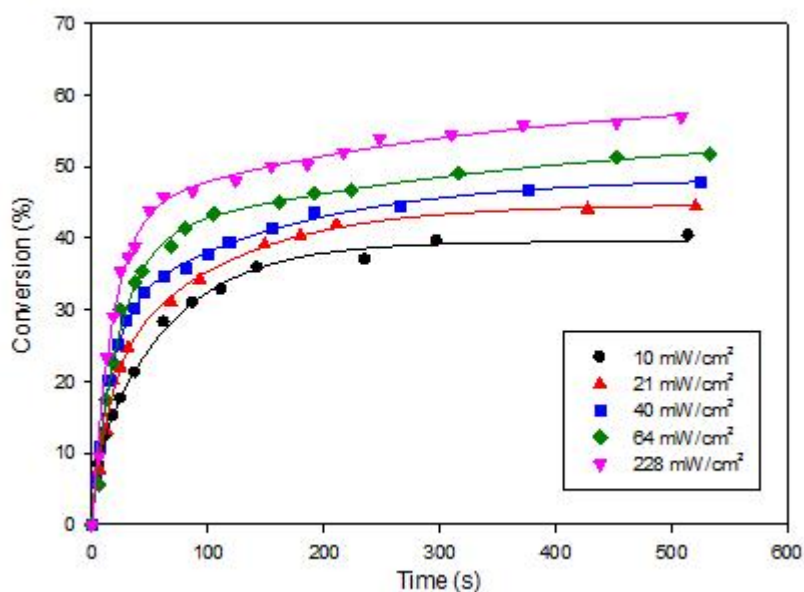


Fig.4. Effect of irradiation on the conversion of the resin
75% Bis-GMA / 25% TEGDMA.

Influence of the temperature

The kinetics of reaction of Bis-GMA / TEGDMA (75/25% by mass) in the presence of 1% by mass of the CQ / DMAEMA (1/1) photoinitiator system was studied at different temperatures (figure 5).

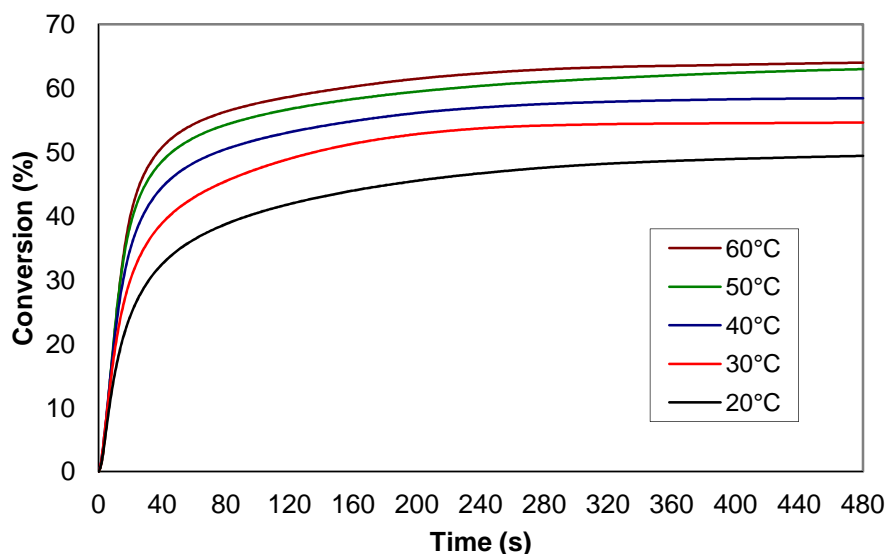


Fig.5. Evolution of the conversion according to the temperature

The existence of a maximum of conversion as a function of the temperature during the photopolymerization of dimethacrylates or of diacrylates has been demonstrated in several works [28, 29]. Andrzejewska places this maximum at about 70 ° C. for a polyether dimethacrylate. The decrease of final conversion generally observed is attributed to a thermal instability of the monomer, to the existence of depolymerization or still to reaction of transfer. In order to avoid these parasitic phenomena, we limited the study to a temperature range between 20 and 60 ° C.

According to the figure 5, the photopolymerization of the 75% Bis-GMA / 25% TEGDMA formulation leads to conversions of less than 100% and which increase with temperature. This incomplete conversion is related to the very rapid vitrification of the system which significantly slows the rate of polymerization. This dependence of the conversion with respect to temperature has been observed in radical polymerization, in particular in the case of the photopolymerization of dimethacrylates or diacrylates having bisphenol A backbones [28]. It is generally accepted that polymerization stops when the Tg of the network being formed approaches the temperature of reaction [30, 31]. This comes true in our case since the Tg of the photocrosslinked materials, measured by Dynamic Mechanical Analysis (DMA), increases with the reaction temperature. 6a, 6b illustrate respectively the evolution of the conversion and of the Tg as a function of the temperature, whereas figure 6c, derived from the two preceding figures, represents the conversion as a function of the Tg. The curve of this figure is very interesting it can allow us to predict the final conversion rate of a sample from the simple knowledge of its Tg.

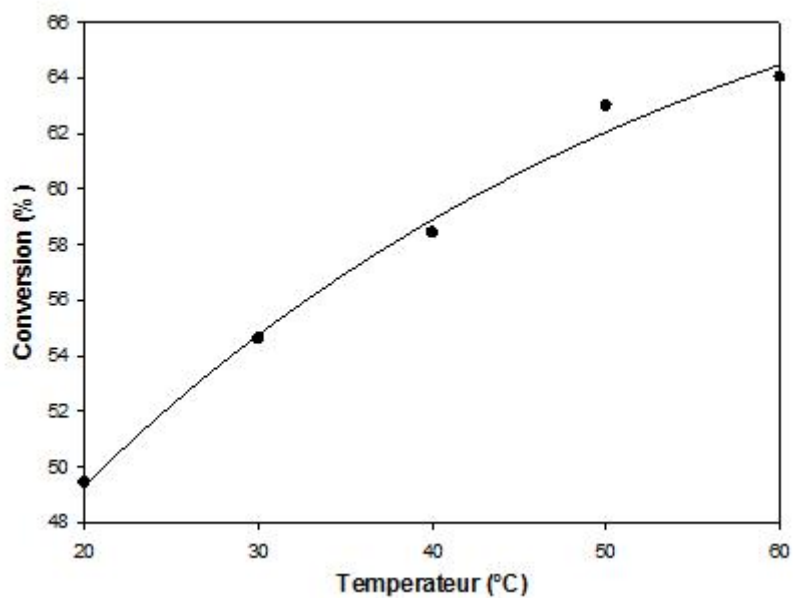


Fig.6a. Evolution of the final conversion according to the temperature

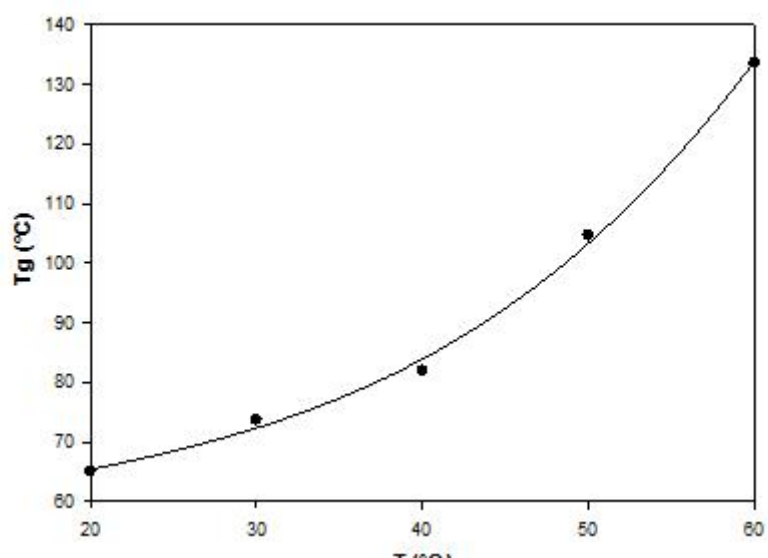


Fig.6b. Evolution of Tg according to the temperature

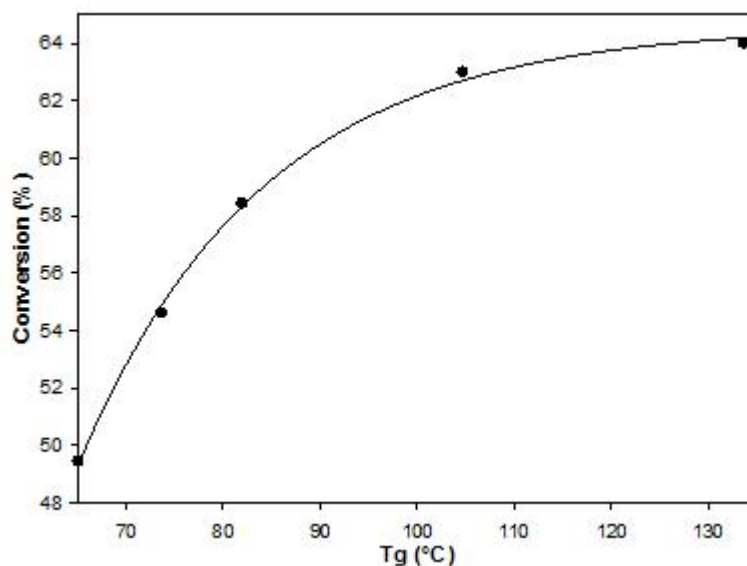


Fig.6c. Evolution of the final conversion according to Tg.

4. CONCLUSION

The influence of various parameters on the evolution of the photopolymerization reaction of the Bis-GMA / TEGDMA formulation was studied by photocalorimetry. The results obtained show for a maximum conversion the existence of an optimal concentration of photoinitiator (CQ / DMAEMA) of 1% (w / w) and a higher luminous intensity ($228 \text{ mW} / \text{cm}^2$). The optimum final conversion remains less than 100% Because of the passage in the glassy state which causes blocking of the reactive species and stops the polymerization.

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